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Movement of Three Herbicides in a Fine Sand Aquifer

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ABSTRACT

In order to determine movement of farm chemicals that might accidentally contaminate underground water supplies, low concentrations of three herbicides and NaNO_3 as a tracer were injected into a sand aquifer through a dual-purpose well. Herbicides used were picloram (4-amino-3,5,6-trichloropicolinic acid), atrazine (2-chloro-4-(ethylamino)-6-(isopropyl-amino)-s-triazine), and trifluralin (α, α, α -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine). Recharge by injection continued for 10 days at an average rate of 81.8 m³/hour. After a 10-day pause, the well was pumped for 12 days to determine if the herbicides and tracer could be recovered. Water samples were pumped from observation wells located 9, 20, and 45 m from the dual-purpose well. Herbicides were detected in the 9- and 20-m distant wells, but none of the herbicides or the tracer was detected in the 45-m distant well. Picloram and atrazine moved freely through the aquifer, but some trifluralin adsorbed to aquifer particles around the well. Although two herbicides moved freely from the point of injection, all of the chemicals were removed from the aquifer by pumping the contaminated water. Ninety-three percent of the NO_3 tracer and more than 90% of each herbicide were recovered with the pumped water. This study indicates that herbicides accidentally injected into a well in a relatively static aquifer can be recovered by pumping. Water could be utilized for irrigation of tolerant crops.

Additional index words: Miscible displacement, Hydrodynamic dispersion.

STORM runoff which recharges groundwater formations may contain small quantities of various agricultural chemicals, including pesticides. Groundwater contamination by pesticides is more likely to occur in an intensively farmed area such as the Texas High Plains where most runoff collects in small playas. In this area, Wiese et al. (9) analyzed runoff water from several fields treated with atrazine (2-chloro-4-(ethylamino)-6-(isopropyl-amino)-s-triazine), propazine (2-chloro-4,6-bis(isopropylamino)-s-triazine), and trifluralin (α, α, α -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine). Maximum concentrations of the three herbicides were 0.04, 0.23, and 0.04 ppm, respectively. Other researchers have found no herbicides or insecticides in playa lake water, but the lake sediments contained some aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo-exo-5,8-dimethanonaphthalene), dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-exo-5,8-dimethano-naphthalene, 85% minimum), and DDT (1,1,1-trichloro-2,2-(*p*-chlorophenyl)ethane) (D. M. Wells, personal communication, 1971). Some of these chemicals could be carried into an aquifer during natural or artificial groundwater recharge.

During the fall of 1969 we measured movement of herbicides in the Ogallala aquifer at USDA Southwestern Great Plains Research Center, Bushland, Tex. For 10 days, water containing three commonly used herbicides and NaNO_3 was injected into the aquifer through a dual-purpose well. Ten days after recharging stopped, the dual-purpose well was pumped until herbicides could not be detected and NO_3 in the water was normal for the aquifer.

Hydrogeology

At Bushland, Tex., the Ogallala aquifer is a fine sand formation containing some silt, clay, and CaCO_3 . The CaCO_3 occurs primarily in nodules and in lenses. The D_{50} sand size is usually less than 0.25 mm, and the uniformity coefficient ranges from about 1.5 to 3.5. D_{10} , D_{50} , and D_{60} are the particle sizes in a granular material such that 10, 50, and 60%, respectively, of the material is smaller. The uniformity coefficient is the ratio of the D_{60} size to the D_{10} size. At Bushland, the groundwater formation is about 66 m thick with the lower 30 m saturated. Cronin (2) described the Ogallala formation in the Southern High Plains of Texas.

The estimated coefficient of transmissivity of the aquifer, derived from pumping and recharge tests, is 250 m²/day/m. The specific yield is probably 0.20 or greater based on water yield-time curves obtained with a neutron moisture meter and the detention time of tracers between a recharge well and observation wells (4).

When the study began, localized pumping and recharging had influenced the water table around the dual-purpose well. The normal gradient for the region is 0.002 m/m toward the southeast (2), but Fig. 1 shows a steeper slope in the recharge area. During June and July 1969, about 37,000 m³ of water was pumped from Well 1, and 24,700 m³ of this water was recharged through an experimental basin 360 m to the west. In addition, the nearest concentration of irrigation wells is to the east and southeast. These sources of recharge and discharge caused the small groundwater mound west of Well 1 and the steep slope to the east.

Wells and Equipment

Well 1 is a dual-purpose well equipped with turbine pump for pumping and injection pipes for recharging. This well was drilled 0.71 m in diameter, cased to the water table with 0.41-m steel pipe, and screened through the saturated sand with 27 m of continuous slot spiral well screen. The well was gravel-packed and developed by pumping and bailing. The turbine pump has a maximum capacity of 227 m³/hour, about twice the sustained yield of the well. Two injection pipes

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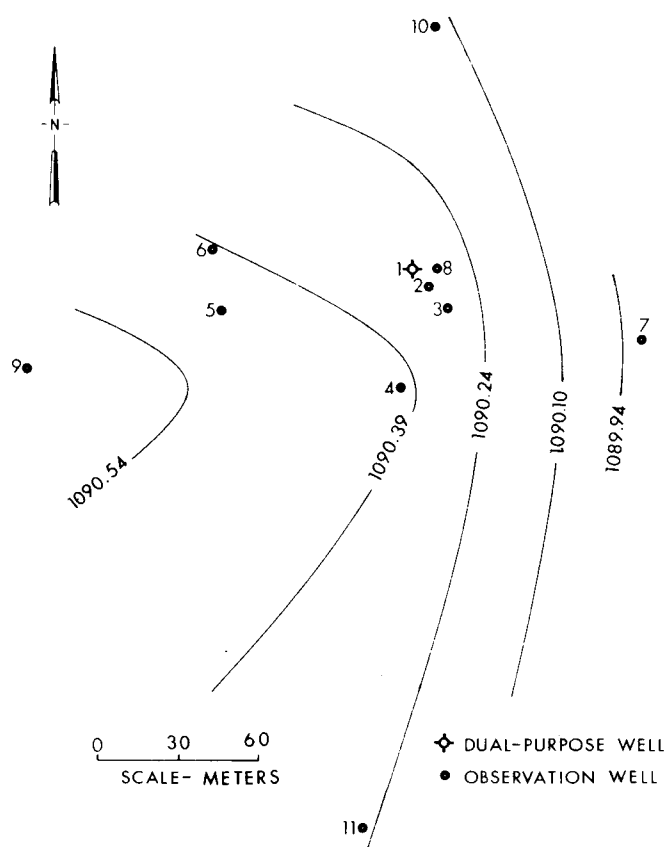


Fig. 1. Plan view of experimental wells and water level contours (meters above MSL) before recharge began on 28 Oct. 1969.

5 cm in diameter are suspended inside the well casing to convey water from the ground surface to the water table without air entrainment. The injection equipment was described previously (7).

Ten observations wells were used in the study (Fig. 1). Well 8 is a 5-cm well with a 1.2-cm long well screen about 6 m below the water table. The others are 15-cm wells screened through the saturated formation. We pumped water samples from Wells 2, 3, 4, and 8 and measured water levels with float-operated recorders in the other wells. Wells 2 and 8 were 9 m from the dual-purpose well, and Wells 3 and 4 were 20 and 45 m, respectively.

Chemical metering equipment was designed to inject 18.9 liters/hour of chemical concentrate into a mixing chamber in the water supply pipeline. We pumped the chemical concentrate from a 568-liter tank into a constant pressure system with a positive bypass flow. An orifice in the constant pressure system delivered 18.9 liters/hour at a pressure of 207,000 N/m², and the bypass flow discharged into the 568-liter tank to agitate the chemicals. The mixing chamber, which consisted of successive right- and left-hand flight auger sections welded inside a 20-cm pipe, thoroughly mixed the chemicals and recharge water before they entered the dual-purpose well. The mixing chamber was described previously (7).

Table 1. Chemicals mixed with the recharge water.

Chemical	Total added — g —	Average concentration — ppm —	Water solubility	Commercial name	Formulation
Picloram	2,469	0.125	430	Tordon 22K	240 gm/l K salt of picloram
Atrazine	25,200	1.28	33	AAtrex	80% wettable powder
Trifluralin	472	0.024	<1	Treflan	480 gm/l emulsifiable concentrate
Nitrate (NO ₃ -N)	199,760	11.85†	730,000	—	Fertilizer grade NaNO ₃ , 16% N

† Includes 1.66 ppm NO₃-N as the average level of NO₃ in the groundwater.

MATERIALS AND METHODS

The herbicides added to the recharge water were picloram (4-amino-3,5,6-trichloropicolinic acid), atrazine, and trifluralin. NaCO₃ was added as a tracer. Table 1 lists the commercial names and formulations for the chemicals. The herbicides are commonly used, or their widespread use is anticipated, and they represent a wide range of solubility and adsorptive capacity (3). Solubilities of unformulated picloram, atrazine, and trifluralin in water are 430, 33 and < 1 ppm, respectively. Formulated products were used, and picloram made a solution, atrazine a suspension, and trifluralin an emulsion in the water mixes. Adsorption of trifluralin, atrazine, and picloram to soil particles is high, moderate, and very low, respectively. With these products, high water solubility is associated with low adsorption to soil and vice versa. Bailey et al. (1) found that 22.7 and 4.3 μmol/g of atrazine and picloram, respectively, were adsorbed to an H-saturated montmorillonite clay.

When Scaff et al. (7, 8) injected NO₃ and tritium into Well 1 during a previous study, there was little NO₃ reduction and both materials proved to be accurate tracers.

Recharge began at 10:20 a.m. on 28 October and continued for 10 days. The chemicals were continuously mixed with the recharge water. The injection rate averaged 81.8 m³/hour and varied within a range of -1.9 to +1.4%. The recharge water came from an irrigation well located 747 m northwest of Well 1. Each day we mixed 1,108 cc of Tordon 22K (picloram), 3,410 gm of AAtrex (atrazine), 106 cc of Treflan (Trifluralin), and 136 kg of NaNO₃ with 473 liters of Ogallala groundwater³. This mixture was transferred to a 1,135-liter tank on a field sprayer for further mixing and was then pumped into the concentrate tank that fed the chemical metering equipment. Table 1 shows the total amount and average concentration of the chemicals injected into Well 1. The chemical feed rate varied considerably during the first 4 days because the chemical pump failed, and the flow rate from a new pump had to be adjusted during the test. After recharge ended, Well 1 remained idle for 10 days to simulate the likely interval between recharging and pumping a dual-purpose well.

Beginning at 1100 hours on 17 November, Well 1 was pumped for 9 days at an average rate of 114 m³/hour and for 3 additional days at an average rate of 109 m³/hour. Pumping rate was reduced on the 10th day because the water level was near the depth where the turbine pump would break suction. Injected water mixed with ground water and was displaced by the natural groundwater flow. Thus, a pumping volume 1.66 times as great as the recharge volume was required to recover most of the injected water as indicated by the NO₃ tracer.

During the pumping and recharge tests, water samples were collected at regular intervals from Wells 1, 2, 3, 4, and 8. At Well 1, recharge water samples were withdrawn just before the water entered the injection pipes in the well casing. During pumping, samples were obtained from a faucet in the pump

³This paper reports the results of research only. Mention of a pesticide in this paper does not constitute a recommendation for use by the USDA nor does it imply registration under FIFRA as amended.

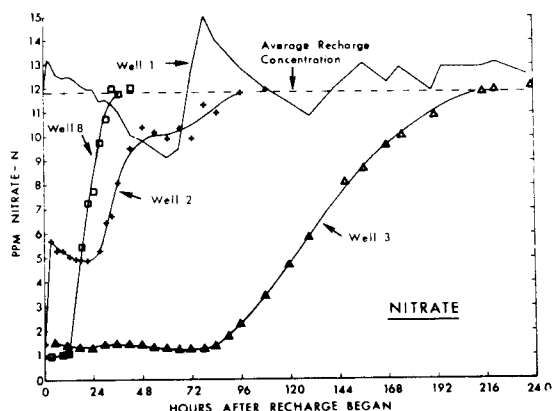


Fig. 2. Nitrate levels in the wells during recharge. Wells 2, 8, and 3 were 9, 9, and 20 m from Well 1.

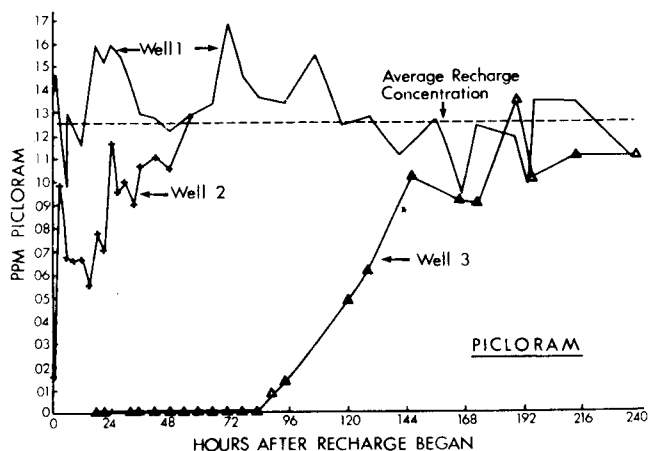


Fig. 3. Picloram levels in the wells during recharge. Wells 2 and 3 were 9 and 20 m from Well 1.

discharge pipe. Well 8, the 5-cm well, was sampled with a piston pump. Before collecting a sample, we pumped the well for 10 min to insure that the water came from the aquifer around the well screen. After the pumping test had been underway for several hours, the cone of depression dropped below the screen of Well 8, and we could not sample this well during the remainder of the test. The 15-cm wells were sampled by lowering a portable submersible pump to the center of the saturated formation, pumping for 30 min, and then collecting the sample. Check samples taken at 6-m depth increments showed that a single sample accurately represented the water from the 15-cm wells.

Nitrate and NO_2 were determined by the automated, colorimetric procedure of Kamphake et al. (5).

Herbicides in the water samples were determined with a Barber-Coleman Model 5360^a gas chromatograph equipped with a radium 226 electron capture detector and a 180-cm spiral glass column. The column contained 10% Dow Corning Silicone Oil 200 on Anakrom ABS 80/90 mesh P³. The carrier gas was repurified N at 138,000 N/m², and the injector, column, and detector temperatures were 235, 190, 210 C, respectively. Standard curves were developed by extracting water with known herbicide concentrations. Herbicide analyses were accurate to about 10% of the concentrations injected into Well 1.

Simple, rapid analyses for atrazine and trifluralin were developed specifically for the study because more than 600 determinations were required. The levels of atrazine and trifluralin injected into Well 1 were selected so that the concentrations gave equal and maximum peak heights with different retention times on the chromatograph recorder. The analyses for the two herbicides consisted of extracting 100 cc of water for 15 min with 100 cc of hexane in an Erlenmeyer flask on a

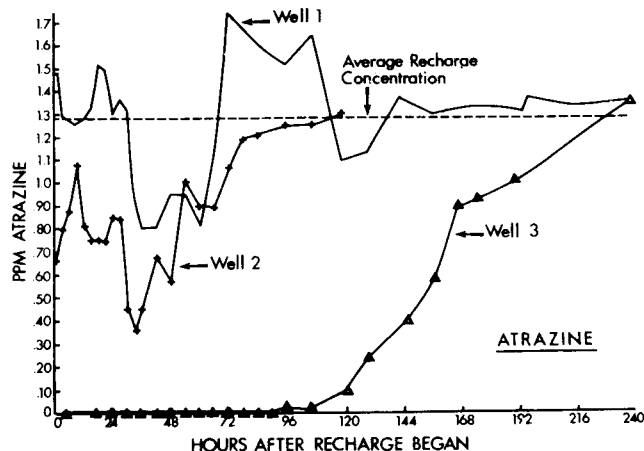


Fig. 4. Atrazine levels in the wells during recharge. Wells 2 and 3 were 9 and 20 m from Well 1.

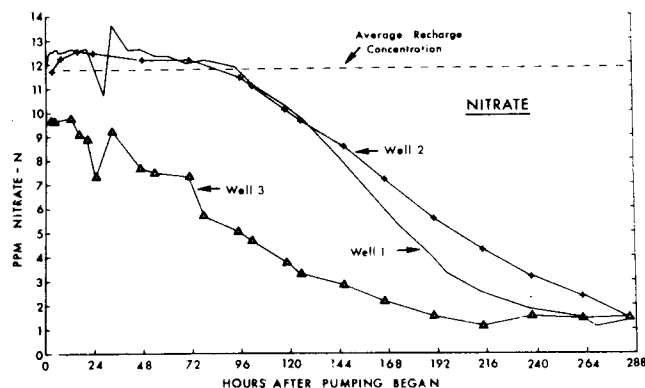


Fig. 5. Nitrate levels in the wells during pumping. Wells 2 and 3 were 9 and 20 m from Well 1.

mechanical stirrer. One to 2 min after stirring ended, the hexane and water separated. Hexane which rose to the top was carefully poured off and concentrated to 5 cc. Five microliters of the concentrate was injected into the gas chromatograph. For trifluralin only the analyses that were made immediately proved to be valid because this herbicide adsorbed to the polyethylene sample containers. We were not aware of this during recharge, but analyses were made immediately after water thawed during the pumping part of the experiment.

The analysis for picloram is a modification of the method proposed by Merkle et al. (6). One hundred cubic centimeters of acidified water was extracted three times with 30 cc of ethyl-ether. The ether was evaporated to dryness, and 10 cc of 12.5% boron trifluoride solution in methyl alcohol was used to convert picloram acid to the methyl ester of picloram. The mixture was evaporated to almost dryness. The few cubic centimeters, including the methyl ester, were washed with 10 cc of water and 10 cc of hexane in a separatory funnel. The hexane layer containing methyl ester of picloram was saved, and 5 μ l aliquots were injected into the gas chromatograph.

RESULTS

Nitrate and herbicide concentrations in the wells during pumping and recharging are shown in Figs. 2 to 8. The recharge data for Well 2 are plotted until the concentration of each chemical increased to the average recharge concentration. Well 8 was sampled primarily to compare the permeability of a thin sand layer with the average permeability of the aquifer.

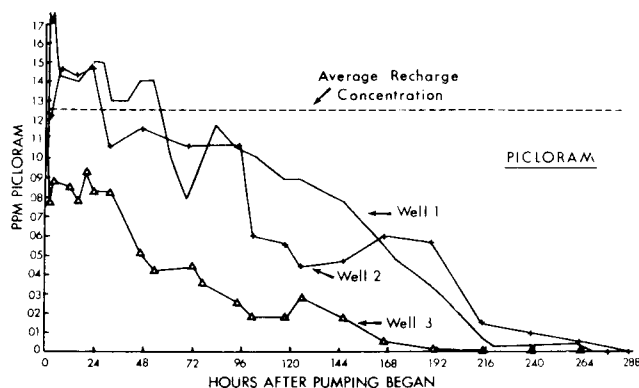


Fig. 6. Picloram levels in the wells during pumping. Wells 2 and 3 were 9 and 20 m from Well 1.

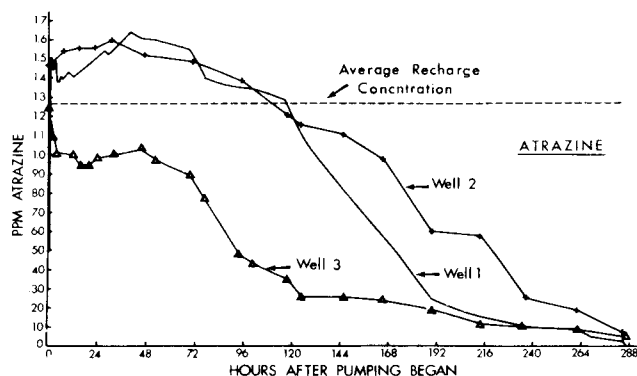


Fig. 7. Atrazine levels in the wells during pumping. Wells 1 and 2 were 9 and 20 m from Well 1.

The tracer illustrates this difference, so only nitrate data from the recharge test are shown for this well.

Recharge Test. Nitrate concentrations in the observation wells generally followed a normal sigmoidal curve as they increased to the average recharge concentration (Fig. 2). Well 2 was an exception because it contained 5.71 ppm $\text{NO}_3\text{-N}$ after only 3 hours of recharge. We believe this was caused by a highly permeable stratum or a thicker gravel pack just above the water table. The screen of Well 1 extended about 1 m into dewatered sand, and recharge water could have moved quickly through this material without having to displace the groundwater. Because of the low NO_3 concentration in Well 1 during the 2nd and 3rd days, Well 2 did not reach the average recharge concentration until 96 hours. In Well 8, the NO_3 level began to increase in 12 hours, and it reached the average recharge concentration in 30 hours. Since the screen in Well 8 is only 1.2 m long, this curve represents a thin stratum of saturated sand rather than the entire aquifer. There was no significant increase of NO_3 in Well 3 until 89 hours. After that, the Well 3 NO_3 level followed a typical breakthrough curve and reached the average recharge concentration after about 210 hours. None of the injected NO_3 was detected in Well 4 which is 45 m from the dual-purpose well.

Picloram moved through the aquifer at approximately the same rate as the NO_3 tracer (Fig. 3). It was

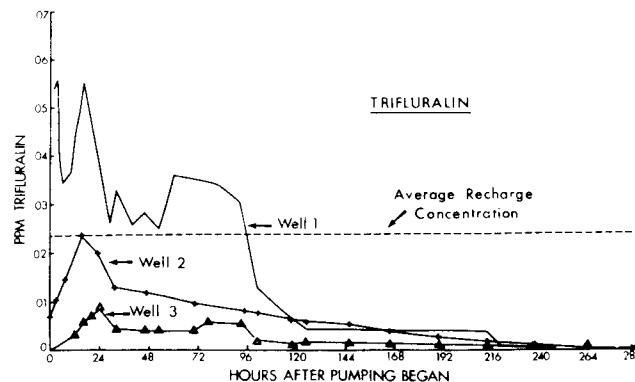


Fig. 8. Trifluralin levels in the wells during pumping. Wells 2 and 3 were 9 and 20 m from Well 1.

detected in Wells 2 and 3 at the same time as NO_3 levels began to increase. In Well 2, picloram level increased to 0.10 ppm in 6 hours and then declined to less than 0.06 ppm before reaching the average recharge concentration after 57 hours. During the last 3 days of recharging, picloram level in Well 3 approached average recharge concentration, but only one sample exceeded this concentration. This probably resulted from the high level of picloram in the injected water at about 18 hours.

Atrazine also moved freely through the aquifer with the recharge water and increased to the average recharge concentration in all wells where tracer was detected (Fig. 4). It was detected at the same time as the NO_3 in Well 2 and about 12 hours after the NO_3 in Well 3. The NO_3 and atrazine curves for Well 2 were similar, but for Well 3, the atrazine curve was displaced about 24 hours to the right of the NO_3 curve indicating some adsorption in the aquifer.

The trifluralin in the samples collected during recharge adsorbed to the polyethylene containers, and the data cannot be interpreted quantitatively. The analyses did show, however, that during the 10 days of recharge some trifluralin reached the three observation wells where the other herbicides were detected.

Pumping Test. Figure 5 shows NO_2 concentrations in Wells 1, 2, and 3 decreasing to background level during the pumping test. In Well 3, NO_3 began to decrease after only 12 hours, but in Wells 1 and 2 it remained nearly constant for 3 days and then began to decrease. Nitrate reached background level after 214 hours in Well 3 and during the 12th day of Wells 1 and 2. With a background level of 1.66 ppm $\text{NO}_3\text{-N}$, calculated NO_3 recovery was 93%.

During the pumping test picloram concentration in all wells declined until each was essentially free of the herbicide (Fig. 6). The picloram level in Well 1 exceeded the average concentration during the first 54 hours of pumping. After that it declined to near the zero level in 220 hours, and at the end of the test Well 1 was free of picloram. Well 3 contained traces of picloram until 216 hours, and Well 2 still contained a trace of picloram at the end of the test. Ninety-three percent of the picloram injected into Well 1 was recovered in the pumped water.

The atrazine levels in Wells 1, 2, and 3 during the pumping test are shown in Fig. 7. During the first 117

hours of pumping atrazine concentration in Wells 1 and 2 exceeded average recharge concentration. After that concentration in Well 1 dropped quickly to 0.25 ppm at 189 hours, and then declined slowly until the end of the test. All three wells contained traces of atrazine at the end of the test. The measurements indicated that slightly more than 100% of the injected atrazine was recovered in the pumped water. This error is within the accuracy limits of the analyses so we conclude that essentially all of the atrazine was recovered by pumping.

Trifluralin levels varied erratically during pumping and were difficult to interpret (Fig. 8). In Wells 2 and 3 trifluralin increased during the first day and then began to decrease. In Well 1, concentration of trifluralin exceeded average recharge concentration during the first 93 hours, then dropped rapidly to less than 0.005 ppm at 125 hours and remained below this level until the end of the test. All of the wells, where trifluralin was detected, contained a trace of the herbicide at the end of the test. The samples collected at Well 1 during pumping indicated a 98% recovery for trifluralin. The above average concentration in the first water pumped indicates that herbicides were being adsorbed to particles in the aquifer. Fast flow rates during pumping would tend to dislodge both sand particles with adsorbed herbicide as well as herbicides from aquifer particles.

The study showed that the herbicides picloram, atrazine, and trifluralin will move through a fine sand aquifer. Picloram, the most soluble and least adsorbed herbicide, was detected in observation wells at the same time as NO_3 . Atrazine also moved freely through the aquifer, but the breakthrough curve for Well 3 was displaced about 24 hours to the right of the NO_3 curve. Quantitative data are not available for trifluralin recharge test, but results of the pumping test suggest that some of the trifluralin was adsorbed to the aquifer particles near the dual-purpose well. During the first 4 days of pumping, trifluralin level in the dual-purpose well exceeded average recharge concentration, but then dropped rapidly to a low level. The trifluralin was probably adsorbed by the aquifer particles near the well and then removed as the water flowed back to the well during pumping.

Natural groundwater flow displaced injected water to the east during the study, but not enough to prevent recovery of most of the water. After 6 days of pumping, the NO_3 concentration in Well 2 was higher than in Well 1. At some time during the later part of the pumping test, concentration of each herbicide was also higher in Well 2 than in Well 1. This suggests that the center of mass of the injected water moved toward Well 2 during the test. A simple calculation shows, however, that the displacement was small in comparison to the distance the injected water moved from Well 1. On Fig. 1, the groundwater contours show an average water table slope of 0.0040 m/m, and a maximum gradient of 0.0054 m/m between Wells 4 and 7. The flow velocity calculated from the maximum gradient, the highest estimate of permeability 25 m/day/m, and the porosity (0.35) is only 3.3 m/month.

If water that is injected through a well is to be recovered from the same well, the ratio of the pumped volume to the recharged volume will increase each day pumping is delayed. Two processes are responsible for this; displacement of injected water by regional groundwater flow and mixing between the injected water and groundwater. After a delay of several weeks to several months, complete recovery through the same well would no longer be practical or possible. In this study, essentially all of the herbicides were recovered after a 10-day pause by pumping 1.66 times the volume of recharged water. Thus, the herbicides could be recovered through a dual-purpose well as long as injected water is not displaced away from the well. The allowable pause will depend on local conditions such as permeability, porosity, and the regional groundwater gradient.

Herbicides which accidentally enter a sand aquifer could be recovered by pumping wells completed in the aquifer. Wiese et al. (9) show that herbicides are not likely to be transported into an aquifer by deep percolation. Herbicide contamination through artificial recharge is more likely because large quantities of water enter the aquifer over a small area. While the recharge water is still concentrated in a small area, it could be pumped from the aquifer through new or existing wells. Irrigating tolerant crops is suggested for disposing herbicide contaminated water.

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